

Ab initio investigations of isopropyl cyanide reaction mechanisms and kinetics of formation on an icy grain model

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Abstract. Isopropyl-cyanide (iso-PrCN) was recently observed in Sagittarius B2 with an abundance higher than its straight-chain structure isomer (n-PrCN). Here we study theoretically by means of [UMP2(full)/aug-cc-pVTZ/Amber] a hybrid *ab initio*/molecular mechanics methodology, the routes leading to its formation on a formaldehyde doped water ice grain model of the interstellar medium. The reaction path and the energetics are calculated, the mechanism is found to be exothermic by ~ 30 kcal/mol and the barrier is ~ 70 kcal/mol. We use the CVT/ZCT semi-classical method to predict the kinetics of the reaction path starting from initially adsorbed HCN and CH₂CHCH₃ molecules colliding from the gas phase over the temperature range [100–500K].

Keywords. Molecular processes, Reaction mechanisms on dust grains.

1. Introduction

A variety of molecules (more than 200) [McGuire \(2018\)](#) have been detected in the interstellar medium (ISM) ([Mackellar \(1940\)](#); [Kaiser \(2002\)](#); [Margulès \(2017\)](#)), among them many radicals and ions containing a CN functional group. Their relevant contribution to the cosmic carbon chemistry and their roles in the chemical evolution of the interstellar and circumstellar media is generally accepted ([Herbst \(2001\)](#)). Since the beginning of the 21st century, fruitful searches have resulted in the detection of 27 different cyanides and isocyanides. Iso-propyl cyanide (iso-C₃H₇CN) a branched alkyl molecule was recently observed. It is the largest and most complex organic molecule found to date - and the only one to share the branched atomic backbone of amino acid that are the building blocks of life. The most stable C₃H₇CN isomer, iso-propyl cyanide was first observed in 2014 with ALMA toward Sgr B2(N), with a fractional abundance with respect to H₂ of $1.3 \pm 0.2 \times 10^{-8}$, leading to an i/n ratio of 0.40 ([Belloche \(2014\)](#)). More recently, both n- and i-propyl cyanide isomers were detected with ALMA towards several emission sources (IRc7 IRc21, MF2 and MF10) in Orion-KL [Pagani \(2017\)](#). The model proposed by [Garrod \(2017\)](#) assumes that the two isomers of propyl-cyanide are formed on grains through different reactions depending on temperature. Our goal in this work is to understand the physical and chemical processes by which iso-C₃H₇CN forms in the ISM. We investigate one possible reaction path for its formation from ab initio energetic point of view as well as from kinetic point of view. We consider the reaction process involving a model of icy dust grain to promote the formation of the iso-PrCN from the reaction

of CH_2CHCH_3 with initially adsorbed HCN molecules. Details of the grain model and electronic structure calculations are given in Section 2 while Section 3 provides the *ab initio* characterisation of the equilibrium geometries and binding energies of the different fragments involved in the reaction path. The energetics of the reaction and insights on the kinetics of formation of iso-PrCN formation are analysed in Section 4. Section 5 provides some concluding remarks.

2. Computational details

2.1. The grain model

In order to prepare a grain model composed of water ice and formaldehydes, a simulation box is built initially placing 20 formaldehyde molecules into a cubic box, filled with 1000 water molecules. We use the Gromacs (Gromacs (2005)) code to perform all molecular dynamics simulations. The first structural property of an interstellar ice to reproduce is the abundance w.r.t. H_2O assumed to be less than 0.05, according to observational/experimental data (Pontoppidan (2004); Boogert *et al.* (2008)). Calculating the densities of our simulation boxes for the water model yield to abundances between 0.05 and 0.04 for the TIP3P model. More precise information on the surface of this ice model can be found in (Kerkeni & Toubin *et al.* (2019)).

2.2. Quantum chemistry computations

We select a layer of amorphous water ice doped with formaldehydes consisting of a parallelepipedic portion ($20\text{\AA} \times 20\text{\AA} \times 7\text{\AA}$) comprised of 219 H_2O and 6 H_2CO . We employ the hybrid QM/MM oniom procedure as implemented in Gaussian 09 (Gaussian (2009)) where the active molecules involved in the reaction process i.e HCN and CH_2CHCH_3 (Marcelino *et al.* 2007) are studied with UMP2(full)/aug-cc-pVTZ (Møller *et al.* (1934); Dunning (1993)), while the rest of the system i.e the icy layer is treated with the Amber force field (Amber (2018)). The icy layer was kept frozen during all calculations.

3. Results

3.1. Fragments

We find that HCN binds to the icy surface more strongly than CH_2CHCH_3 with a binding energy of 242 kcal/mol. We consequently initiated the reaction process by the reactive collision of one single gaseous CH_2CHCH_3 molecule with an already adsorbed HCN molecule on the icy layer which lead to a binding energy of 10.9 kcal/mol. The reactive collision of propene with HCN on the icy surface resulted in a strongly bound vdW complex (~ 253 kcal/mol). Upon the encounter of the reactants, reorientation of the molecules follows to form the vdW complex for which the N-C-C angle is $\sim 90^\circ$, and gradual approach of the two molecules results in a shortening of the C-C bond from ~ 3 to 1.46 (the first C belongs to HCN and the second C is the central carbon of propene), the bending angle of the HCN molecule varies from 180° to 114° . The search of the transition state (see Figure 1) corresponds to the geometrical configuration where the hydrogen in HCN is transferred to the ethyl group of propene. At the transition state the CN bond is elongated by 0.08 with respect to the vdW's one.

3.2. Energetics

The first reaction step consists of gas phase HCN and propene sequential adsorption on the icy layer barrierless (R1). Upon adsorption on the surface a strongly bound vdW complex may be formed (R2), upon appropriate orientation of the molecules, the mecha-

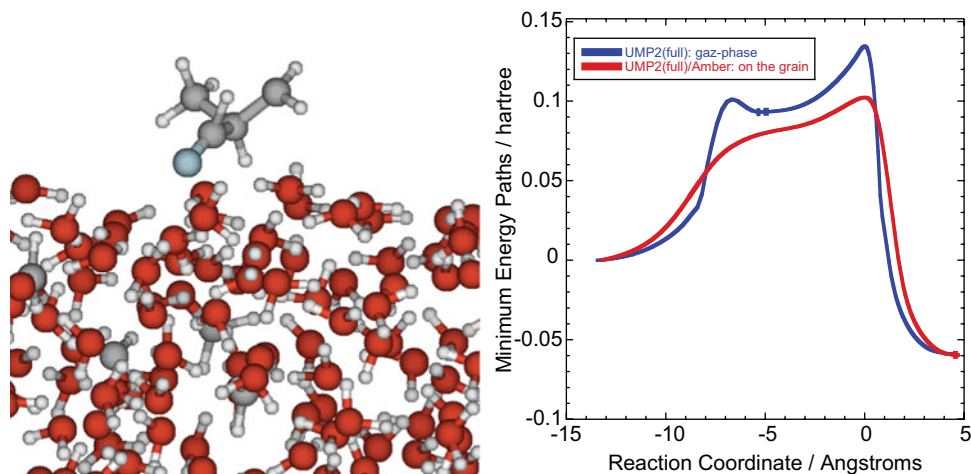


Figure 1. Transition state geometry of the H transfer reaction mechanism above the icy layer (left panel). Comparison of the classical potential energy (V_{MEP}) on the icy layer, and the one obtained in the gas phase (right panel).

nism (R3) involves a single reaction transition state following H transfer from the formed $\text{HCN}(\text{CH}_2\text{-CH-CH}_3)$ complex to the ethyl group of propene. Finally iso-PrCN is formed adsorbed on the icy layer and then ejected into the gas phase (4.06 kcal/mol) (R4). The formation of iso-PrCN is found to be exothermic by 30.8 kcal/mol (27.62 ZPE corrected), while the total exothermicity of the reaction amounts to -279.88 kcal/mol. The activation barrier for the H transfer reaction is 70.83 kcal/mol (70.37 ZPE corrected) would easily be overcome by the high binding energy gained by the two species HCN and CH_2CHCH_3 and would possibly lead to the formation of vibrationally excited iso-PrCN molecules.

4. Reaction mechanisms

4.1. Minimum energy path

In the present work we have computed the minimum energy path for iso-PrCN formation following the H transfer process. The reactants correspond to the vdW of adsorbed CH_2CHCH_3 and HCN species while the product being the physisorbed iso-PrCN. The Minimum Energy Path (MEP) was determined from Intrinsic Reaction Coordinate (IRC) calculations (Hratchian & Schlegel 2005), as implemented in Gaussian. The energies were vibrationally corrected adding the zero point vibrational energy (ZPE). Figure 1 displays the variation of the classical potential energy (V_{MEP}) as a function of the reaction coordinate (s), for comparison purposes the MEP obtained for gas phase reaction of HCN and propene is also displayed (Kerkeni and Senent *et al.* (2019)). From the figure we can clearly see that the reaction on the icy surface is quite different from that in gas phase, indeed we notice that the latter is showing two transitions states, the first attributed to the C-C bond formation while the second corresponds to the H transfer step. On the icy surface the first step occurs without any barrier. Besides, we clearly see from the figure that the height of the classical barrier has been reduced on the surface of this ice model from 83.82 kcal/mol to 70.83 kcal/mol. That is the ice model yields a noticeable stabilization of the gas-phase Transition States (TSs) with respect to the effect on the minima.

Table 1. CVT/ZCT rate constants for the iso-PrCN formation on the icy-model, powers of 10 in parentheses.

T[K]	100	200	300	400	500
k(T) [s ⁻¹]	1.678(-45)	1.034(-45)	1.084(-40)	3.138(-28)	9.698(-21)

4.2. Kinetic study: formation processes

The computation of rate constants for iso-PrCN formation was performed over the temperature range [100 – 500 K] using the (POLYRATE (2016)) code version 2016-2A. Different semiclassical methods could be used to evaluate transmission coefficients $\kappa(T)$ depending on the degree of coupling between the MEP and other degrees of freedom through the MEP curvature, here we use the CVT/ZCT procedure detailed elsewhere (Skodje *et al.* (1981)). Geometries, gradients and Hessians along the minimum reaction path were computed using the UMP2(full)/aug-cc-PVTZ/Amber method. Quantum mechanical vibrational partition functions are evaluated by the harmonic approximation, by summing Boltzmann factors using quantum energy levels. Table 1 shows the rate constants computed for selected temperatures. As can be seen the rate constants increase with temperature due to the relatively high energetic barrier. However quantum tunneling is quite large at T = 250K ($\kappa \sim 1000$), and decreases at T = 500 K to $\kappa \sim 1.3$.

Even though the predicted rate constants appear to be very low, the exothermicity of the reaction path on the icy-model that amounts to (-15499 K) would efficiently catalyse iso-PrCN(gas) formation. The total exothermicity of producing iso-PrCN(gas) following this reaction path via the double physisorption mechanism would be -140845 K (i.e. -121866 K -5487K -15535K + 2043 K). The activation barrier for HCN + CH₂CHCH₃ recombination would easily be overcome by the high binding energy gained by the two physisorbed reactants even if assuming 50 % of the internal energy would be dissipated into the icy surface. We are currently investigating reaction mechanisms involving radical addition and we found that these reactions are barrierless and highly exothermic leading to expected fast reactive processes for the formation of propyl cyanide products. The kinetics of such diradical reactions is under study.

5. Summary and Conclusion

In summary, we use a realistic model of an amorphous water ice doped with formaldehydes according to an observed density. We employ a hybrid QM/MM methodology to study the bimolecular reactivity of HCN and propene species towards iso-PrCN formation. We carried out global optimisations of the gaseous species keeping the icy surface atoms frozen. The energetics show that the reaction is exothermic and has a barrier height quite large. CVT/ZCT rate constants were computed for various temperatures in the range [100–500 K]. These findings would allow the H transfer mechanism fully justify the feasibility of the reaction process on the icy surface towards the observation of iso-PrCN, probably in the cold and certainly in warm gas sources. In the future, it would be interesting to consider studying the formation of iso-C₃H₇CN and n- C₃H₇CN on selected models of icy grains and from different types of radical-radical reactions in order to explore reaction energetics and the most favorable routes for their formation in typical physical conditions relevant to the ISM where they were detected.

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